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[DOCUMENT NAME] CLAIMS

[Claim 1] A separator for an electric double layer capacitor, characterized in that said separator is composed of an ultrafine fibrous aggregate prepared by an electrostatic spinning process, an average fiber diameter of ultrafine fibers constituting said ultrafine fibrous aggregate is 1 μm or less, and a thickness of said ultrafine fibrous aggregate is 20 μm or less.

[Claim 2] The separator for an electric double layer capacitor according to claim 1, characterized in that said ultrafine fiber is composed of at least one resin selected from the group consisting of polyacrylonitrile, polyvinylidene fluoride, polyimide, nylon, polystyrene, polyurethane, polyethylene glycol, and polyvinyl alcohol.

[Claim 3] The separator for an electric double layer capacitor according to claim 1 or 2, characterized in that a tensile strength per 1 g/m^2 in mass per unit area is 0.15 N/5 mm width or more in at least one direction of said ultrafine fibrous aggregate.

[Claim 4] An electric double layer capacitor comprising said separator according to any one of claims 1 to 3.

[DOCUMENT NAME] Specification
[TITLE OF THE INVENTIONS] SEPARATOR FOR ELECTRIC DOUBLE
LAYER CAPACITOR AND ELECTRIC DOUBLE LAYER CAPACITOR
CONTAINING SAME
[TECHNICAL FIELD]

[0001]

The present invention relates to a separator for an electric double layer capacitor and an electric double layer capacitor containing the same. More particularly, the present invention relates to a separator preferably applicable to a thin electric double layer capacitor, and a thin electric double layer capacitor.

[BACKGROUND ART]

[0002]

An electric double layer capacitor has a relatively large capacity and a long life-time, and allows a quick charge and discharge. Therefore, it has been used not only in conventional applications, such as a leveling of an electric power source or an absorption of noise, but also in a memory-backup power source for a personal computer, or as an auxiliary or substitutive source of a secondary battery. Recently, the electric double layer capacitor is expected to be used as a secondary battery for an electric vehicle.

[0003]

The electric double layer capacitor has a structure wherein a pair of electrodes is immersed in an ionic solution. When a voltage is applied to the electric double layer capacitor, ions having a charge opposite to that of each electrode are distributed around each electrode to form layers of ions, whereas, in the electrodes, charges opposite to the outside ions are accumulated. Then, if a load is connected between the electrodes, the charges in the electrodes are discharged, and at the same time the ions distributed around the electrodes move away therefrom so that the capacitor is returned to a neutralized state.

[0004]

If a pair of the electrodes is brought into contact with each other in the electric double layer capacitor, it becomes difficult to form the ion layer around the electrodes. Therefore, a separator is usually placed between the electrodes. The separator is required to have a property of avoiding a short circuit between the electrodes

as above, and further a good property of holding an electrolyte and an ionic permeability.

[0005]

If a thin separator is used as a separator for the electric double layer capacitor, the electric double layer capacitor can be thinned. Thus, porous membranes were proposed as the separator. For example, a separator made of a polyimide porous film having nonlinear fine holes was proposed (patent reference 1).

[0006]

[patent reference 1] Japanese Unexamined Patent Publication (Kokai) No. 2003-229329 (Claim 1)

[DISCLOSURE OF THE INVENTION]

[PROBLEMS TO BE SOLVED BY THE INVENTION]

[0007]

The porous film disclosed in patent reference 1 does not have a sufficient holding electrolyte property. Further, if the thickness is reduced to enhance an ionic permeability, a property of preventing a short circuit becomes lower. If the thickness is increased to enhance the property of preventing a short circuit, the ionic permeability is deteriorated, and at the same time, the electric double layer capacitor becomes thicker. This does not satisfy both the ionic permeability and the property of preventing a short circuit, at the same time.

[0008]

The present invention has been completed to solve the above problems, and the object of the present invention is to provide a separator for the electric double layer capacitor, having an excellent holding electrolyte property, and capable of satisfying both a property of preventing a short circuit and an ionic permeability, and an electric double layer capacitor containing the same.

[MEANS FOR SOLVING THE PROBLEMS]

[0009]

The present invention set forth in claim 1 is a separator for an electric double layer capacitor, characterized in that the separator is composed of an ultrafine fibrous aggregate prepared by an electrostatic spinning process, an average fiber diameter of ultrafine fibers constituting the ultrafine fibrous aggregate is 1 μm

or less, and a thickness of the ultrafine fibrous aggregate is 20 μm or less.

[0010]

The present invention set forth in claim 2 is the separator for an electric double layer capacitor according to claim 1, characterized in that the ultrafine fiber is composed of at least one resin selected from the group consisting of polyacrylonitrile, polyvinylidene fluoride, polyimide, nylon, polystyrene, polyurethane, polyethylene glycol, and polyvinyl alcohol.

[0011]

The present invention set forth in claim 3 is the separator for an electric double layer capacitor according to claim 1 or 2, characterized in that a tensile strength per 1 g/m^2 in mass per unit area is 0.15 N/5 mm width or more in at least one direction of the ultrafine fibrous aggregate.

[0012]

The present invention set forth in claim 4 is an electric double layer capacitor comprising the separator according to any one of claims 1 to 3.

[EFFECTS OF THE INVENTION]

[0013]

The present invention set forth in claim 1 is composed of a dense ultrafine fibrous aggregate prepared by an electrostatic spinning process, wherein an average fiber diameter of ultrafine fibers constituting said ultrafine fibrous aggregate is 1 μm or less. Therefore, a property of preventing a short circuit is excellent, and a holding electrolyte property is excellent because many very fine pores are formed. Further, because the thickness is very thin, that is, 20 μm or less, an ionic permeability is excellent.

[0014]

According to the present invention set forth in claim 2, the separator is not affected by the electrolyte, and thus, the excellent properties of preventing a short circuit and of holding an electrolyte are maintained for a long time.

[0015]

According to the present invention set forth in claim 3, a mechanical strength is excellent, and thus, the electric double layer capacitor can be easily prepared.

[0016]

The present invention set forth in claim 4 has a low internal resistance, and a long life-time.

[MEANS FOR SOLVING THE PROBLEMS]

[0017]

The separator for an electric double layer capacitor (hereinafter simply referred to as "separator") according to the present invention consists of an ultrafine fibrous aggregate which is prepared by an electrostatic spinning process, and is composed of ultrafine fibers having an average fiber diameter of 1 μm or less. Therefore, the pore size is small and a distribution of the pore sizes is narrow, and as a result, the present separator has excellent properties of preventing a short circuit, and of holding an electrolyte.

[0018]

The smaller the average fiber diameter of the ultrafine fibers, the more excellent the properties of preventing a short circuit, and of holding an electrolyte are. Therefore, the average diameter of the ultrafine fibers is preferably 0.8 μm or less, more preferably, 0.6 μm or less. There is no lower limit of the average fiber diameter of the ultrafine fibers, but it is appropriately around 1 nm. The term "fiber diameter" as used herein means a diameter of a cross section of a fiber, which diameter can be measured in an electron microscopic picture of the separator. When the shape of the cross section of the fiber is not a circle, a diameter of a circle having an area the same as that of the noncircular cross section is regarded as the fiber diameter. The term "average fiber diameter" as used herein means an arithmetic average of fiber diameters of 50 or more fibers.

[0019]

The separator of the present invention is composed of the ultrafine fibrous aggregate prepared by an electrostatic spinning process, and thus, the fiber diameters of the ultrafine fibers are uniform, the pore sizes are small, and a distribution of the pore sizes is narrow. Therefore, it has excellent properties of preventing a short circuit, and of holding an electrolyte. More particularly, a ratio (D_d/D_a) of a standard deviation (D_d) of fiber diameters of ultrafine fibers constituting the separator to an average fiber diameter (D_a) of ultrafine fibers constituting the

separator is preferably 0.25 or less. The small value of the ratio (Dd/Da) means that the fiber diameters of the ultrafine fibers are uniform. In view of the excellence of the properties of preventing a short circuit and of holding an electrolyte, the ratio (Dd/Da) is preferably 0.20 or less. When all the ultrafine fibers have same fiber diameter, the standard deviation becomes 0. Thus, the lower limit of the ratio (Dd/Da) is 0. The "standard deviation (Dd) of a fiber diameter" as used herein means a value calculated from fiber diameters (χ) measured for discrete ultrafine fibers by the following equation:

Standard deviation (Dd) = $\{(n\sum\chi^2 - (\sum\chi)^2)/n(n-1)\}^{1/2}$
wherein "n" stands for the number (50 or more) of the ultrafine fibers whose diameters are measured.

[0020]

A fiber length of the ultrafine fibers constituting the separator of the present invention is not limited. When prepared by an electrostatic spinning process, the fibers are usually continuous fibers. It is preferable that the ultrafine fibers are continuous, because the fibers are rarely dropped out during the production of the electric double layer capacitor. When the ultrafine fibers are continuous as above, the fiber diameter is measured on the basis of an electron microscopic picture of a cross section of the separator in a thickness direction. The average fiber diameter and the standard deviation of the fiber diameter are calculated on the basis of the fiber diameters of 50 or more ultrafine fibers in the electron microscopic picture. The fibers may be made discontinuous by, for example, intermittently discharging a fiberizable liquid.

[0021]

The ultrafine fibers constituting the separator of the present invention may be formed from a resin which is inert by electrolyte in the electric double layer capacitor, and is preferably composed of, not limited to, for example, at least one resin selected from polyacrylonitrile, polyvinylidene fluoride, polyimide, nylon, polystyrene, polyurethane, polyethylene glycol, or polyvinyl alcohol. Of these resins, polyacrylonitrile is preferable, because an ultrafine fibrous aggregate made of the ultrafine fibers having an average fiber diameter of 1 μm or less can be reliably prepared by an electrostatic spinning process.

[0022]

The separator of the present invention may be formed from the ultrafine fibrous aggregate of the ultrafine fibers as above, and the thickness is 20 μm or less to obtain an excellent ionic permeability. The thickness is more preferably 15 μm or less. If the thickness of the ultrafine fibrous aggregate is too thin, there is a tendency to affect the properties of preventing a short circuit and a holding electrolyte even if the separator is made of the ultrafine fibers. The entire thickness is preferably 5 μm or more. The term "thickness" as used herein means an arithmetic average of 10 randomly selected points measured in accordance with JIS C2111 5.1(1), using an outside micrometer (0 to 25 mm) defined in JIS B 7502: 1994.

[0023]

In the separator of the present invention, a tensile strength per 1 g/m^2 in mass per unit area is preferably 0.15 N/5 mm width or more in at least one direction of the separator, so that the separator has a mechanical strength which allows an easy production thereof. The stronger the tensile strength per 1 g/m^2 in mass per unit area, the easier it is to produce an electric double layer capacitor. Therefore, the tensile strength is preferably 0.5 N/5 mm width or more. There is no upper limit. If an electric double layer capacitor is manufactured in a wound form, a tension is applied to the separator mainly in a longitudinal direction thereof. Therefore, the above-defined value of the tensile strength is preferably satisfied in the longitudinal direction. The "tensile strength per 1 g/m^2 in mass per unit area" means a quotient obtained by dividing a tensile strength with a mass per unit area, and the "tensile strength" means a value obtained by fixing a rectangular separator sample prepared by cutting the separator into a form having a length of 5 cm in a direction perpendicular to a measuring direction and a length of 20 cm in the measuring direction, between the chucks (distance between the chucks: 10 cm) of a tensile strength tester (Orientec Co., Ltd., Tensiron UTM-III-100), pulling the sample at an extending rate of 50 mm/min, and calculating a force required to break the separator. The "mass per unit area" means a mass per 1 m^2 .

[0024]

In the separator of the present invention, the ultrafine fibers are preferably bonded to each other with pressure so that the separator can have an excellent tensile strength as above. The bonding of the ultrafine fibers to each other with pressure is advantageous in that an ionic permeability is not prevented by a formation of a film, in contrast with the case where the ultrafine fibers are fused to each other. Further, it is also advantageous in that an internal resistance can be lowered, and an energy density per a certain volume can be raised. The "bonding with pressure" as used herein means a state wherein the ultrafine fibers are firmly attached to each other by pressing the fibers without heating, or with heating at a temperature less than a softening point of the ultrafine fibers.

[0025]

The mass per unit area of the separator of the present invention is not limited, but preferably 1 to 10 g/m², more preferably 1 to 5 g/m², still more preferably 1 to 3 g/m², in view of the excellent properties of holding an electrolyte, preventing a short circuit, and an ionic permeability. The apparent density of the separator is not particularly limited, but is preferably 0.1 to 0.8 g/cm³. If the apparent density is less than 0.1 g/cm³, tendencies occur that a handling property is deteriorated, pore sizes become larger, a distribution of pore sizes becomes wider, the properties of preventing a leakage of an electrical current and a short circuit are affected, and the holding electrolyte property is lowered. Thus, the apparent density is more preferably 0.2 g/cm³ or more. On the contrary, if the apparent density is more than 0.8 g/cm³, tendencies occur that a porosity is too low, an ionic permeability is affected, and the holding electrolyte property is lowered. Thus, the apparent density is more preferably 0.7 g/cm³ or less, still more preferably 0.65 g/cm³ or less. The "apparent density" means a quotient obtained by dividing a mass per unit area with a thickness.

[0026]

It is preferable that the ultrafine fibers constituting the separator of the present invention are not substantially entangled with each other. When the ultrafine fibers are not substantially entangled, the separator can have a small

pore size, and a narrow distribution of pore sizes, and excellent properties of preventing a short circuit and of holding an electrolyte. In other words, if a fluid stream such as a water jet is applied so as to entangle the ultrafine fibers, the ultrafine fibers are rearranged so that the configuration of the ultrafine fibers is disturbed, the pore sizes are increased, and the distribution of the pore sizes is widened. On the contrary, when the ultrafine fibers are not entangled, the configuration of the ultrafine fibers is not disturbed so that the separator having small pore sizes and a narrow distribution of the pore sizes may be easily realized. The expression "the ultrafine fibers are not substantially entangled" as above means a state wherein an entangling treatment is not carried out after forming the ultrafine fibrous aggregate.

[0027]

More particularly, a mean flow pore size of the separator is preferably as small as 1 μm or less, more preferably 0.8 μm or less, still more preferably 0.7 μm or less. In the separator of the present invention, a maximum pore size is 3 times or less (preferably 2.7 times or less) of the mean flow pore size. In an ideal embodiment, a maximum pore size is one time the mean flow pore size, that is, all the pore sizes are identical to each other. The "mean flow pore size" means a value obtained in accordance with a method described in ASTM-F316, for example, a value measured by a mean flow point method using a polometer (Perm Polometer, PMI). The "maximum pore size" means a value measured by a bubble point method using a polometer (Perm Polometer, PMI).

[0028]

The separator of the present invention consists of the ultrafine fibrous aggregate which is prepared by an electrostatic spinning process, and is composed of ultrafine fibers having an average fiber diameter of 1 μm or less. The separator may be prepared, for example, by (1) a fiberizing step comprising discharging a fiberizable solution containing resins forming the ultrafine fibers from nozzles, and at the same time applying an electrical field to the discharged fiberizable solution for fiberization, and (2) a collecting step comprising collecting the fiberized

fibers on a collector to form the ultrafine fibrous aggregate.

[0029]

More particularly, the fiberizable solution is prepared at the beginning. The fiberizable solution is a solution prepared by dissolving the resin forming the ultrafine fibers for the separator in a solvent. As the resin for the ultrafine fibers, for example, one or more of the above-mentioned resins may be used. The solvent may be selected in accordance with the resin to be used, and thus is not limited. There may be mentioned as the solvent, for example, water, acetone, methanol, ethanol, propanol, isopropanol, tetrahydrofuran, dimethyl sulfoxide, 1,4-dioxane, pyridine, N,N-dimethylformamide, N,N-dimethylacetoamide, N-methyl-2-pyrrolidone, acetonitrile, formic acid, toluene, benzene, cyclohexane, cyclohexanone, carbon tetrachloride, methylene chloride, chloroform, trichloroethane, ethylene carbonate, diethyl carbonate, propylene carbonate, or the like. The solvent may be used alone, or a mixture of two or more solvents may be used.

[0030]

The fiberizable solution is prepared by dissolving the resins as above in one or more solvents. The concentration of the resin or resins may vary with a composition of the resins used, a molecular weight of the resin or resins, and/or the solvent or the solvents, and thus is not limited. However, in view of the applicability to the electrostatic spinning, the concentration corresponds to a viscosity of preferably 10 to 6000 mPa·s, more preferably 20 to 5000 mPa·s. If the viscosity is less than 10 mPa·s, the viscosity is too low to exhibit a sufficient stringiness, and thus it is difficult to obtain fibers. If the viscosity is more than 6000 mPa·s, the fiberizable solution becomes difficult to be drawn, and it is difficult to obtain fibers. The term "viscosity" as used herein means a value measured at 25°C by an apparatus for measuring viscosity at a shear rate of 100 s⁻¹.

[0031]

The fiberizable solution is supplied to nozzles and discharged therefrom, and at the same time an electrical field is applied to the discharged fiberizable solution for fiberization. The diameter (internal diameter) is

preferably about 0.1 to 2 mm so that an average fiber diameter of the ultrafine fibers can be easily adjusted to 1 μm or less. The nozzle may be made from a metal or non-metal material. When the nozzle is made from a metal, it can be used as one of the electrodes to apply an electrical field to the discharged fiberizable solution. When the nozzle is made from a non-metal material, an electrode is installed in the nozzle and an electrical field can be applied to the discharged fiberizable solution.

[0032]

The fiberizable solution is discharged from the nozzles as above, and an electrical field is applied to the discharged fiberizable solution so that the solution is drawn and fiberized. The electrical field may vary with the average fiber diameter of the ultrafine fibers, a distance between the nozzle and the collector, the solvent of the fiberizable solution, the viscosity of the fiberizable solution, and the like, and thus is not limited. However, the electrical field is preferably 0.2 to 5 kV/cm so that the average fiber diameter of the ultrafine fibers can be adjusted to 1 μm or less. There is a tendency that the average fiber diameter of the ultrafine fibers is thinned with the increase of the electrical field applied. However, the electrical field exceeding 5 kV/cm is not preferable, because an air dielectric breakdown is liable to occur. When the electrical field is less than 0.2 kV/cm, it is difficult to obtain a fibrous shape.

[0033]

As above, an electrical field is applied to the discharged fiberizable solution, and thus static charges are accumulated in the fiberizable solution. The solution is electrically attracted by the electrode placed on the side of the collector, and stretched to be fiberized. The fibers are electrically drawn, and thus, the rate of the fibers coming close to the collector is accelerated by the electrical field so that the ultrafine fibers having a small average fiber diameter are obtained. Further, it is considered that the fibers are also thinned by evaporation of the solvent, and a repulsive force generated by an elevated static density causes cleavages of the fibers so that the ultrafine fibers having a small average fiber diameter are obtained.

[0034]

The electrical field as above can be applied by, for example, generating a difference in potential between the collector and the nozzle, that is, the nozzle per se in the case of the metal nozzle, or the electrode in the nozzle in the case of the non-metal nozzle, such as a glass or resin nozzle. For example, the difference in potential can be generated by applying a voltage to the nozzle and grounding the collector. Alternatively, the difference in potential can be generated by applying a voltage to the collector and grounding the nozzle. An apparatus for applying a voltage is not limited. For example, a DC high-voltage generator or Van De Graff electrostatic generator may be used. A voltage applied is not limited, so long as it may generate the electric field strength as above, but is preferably about 5 to 50 kV.

[0035]

Subsequently, the collecting step (2) for accumulating the fiberized ultrafine fibers on the collector to form the ultrafine fibrous aggregate is carried out. The collector used in the collecting step is not limited so long as it can accumulate the ultrafine fibers. For example, a non-woven fabric, woven fabric, knitted fabric, net, flat plate, drum, or belt made of an electrically conductive material such as metal or carbon, or an electrically non-conductive material such as an organic polymeric material may be used as the collector. When the collector is used as an electrode as above, it is preferably made of an electrically conductive material such as metal having a specific resistance of $10^9 \Omega$ or less. On the other hand, when an electrically conductive material is positioned as a counter electrode behind the collector (when observed in a direction from the nozzle to the collector), the collector is not necessarily made of an electrically conductive material. When such a counter electrode is placed behind the collector as above, the collector may be brought into contact with the counter electrode, or may be separated from the counter electrode.

[0036]

The ultrafine fibrous aggregate which is the separator of the present invention may be produced by the above steps, and may be subjected to a densifying step comprising

densifying the ultrafine fibrous aggregate with pressure. The densifying step is carried out so that the tensile strength and smoothness are enhanced, the mean flow pore size is adjusted to 1 μm or less, the maximum pore size is adjusted to not more than 3 times the mean flow pore size, and the thickness is adjusted to 20 μm or less. The pressure applied in the densifying step is not particularly limited, but preferably the densifying step is carried out at a linear pressure of 5 N/cm or more so that the tensile strength per mass per unit area 1 g/m^2 can be increased to 0.15 N/5mm width or more.

Preferably, the ultrafine fibrous aggregate is heated when pressed so that the tensile strength can be effectively increased. When heated as above, the ultrafine fibrous aggregate can be heated before being pressed or heated and pressed at the same time. In each case, the ultrafine fibrous aggregate is heated preferably at a temperature of less than the softening temperature of the ultrafine fibers, more preferably at a temperature lower by 10°C or more than the softening temperature of the ultrafine fibers, still more preferably at a temperature lower by 20°C or more than the softening temperature of the ultrafine fibers. The densifying step can be carried out by, for example, a calendar roll or a thermal calendar roll. The "softening temperature" as used herein means a temperature giving an initial point of an endothermal curve of fusion in a DSC curve obtained by a heat flux differential scanning calorimetry (DSC, elevating temperature 10°C/min) defined in JIS K 7121.

[0037]

After the densifying step, the solvent of the fiberizable solution is preferably removed by heating at a temperature above the temperature at the densifying step but lower by 50°C or more than the pyrolysis temperature of the ultrafine fibers. By the heating as above, the tensile strength of the separator can be increased. As a result, the electric double layer capacitor can be more easily manufactured. The "pyrolysis temperature" means a temperature when a mass of a test sample is reduced by 5% in a thermogravimetric analysis defined in JIS K 7120.

[0038]

The electric double layer capacitor of the present invention contains the above-mentioned separator, and has a low internal resistance and a long life time. Particularly, when the resins forming ultrafine fibers of the above separator have a melting point or a carbonizing temperature of 300°C or more, a drying step can be carried out after assembling the electrodes group from components for capacitor. Therefore, it is advantageous when an organic electrolyte is used.

[0039]

The capacitor of the present invention is same as the conventional capacitor except that it contains the above-mentioned separator. For example, a thin metal plate such as a thin aluminum plate or a thin platinum plate can be used as a collecting electrode. As the electrode, an electrode prepared by mixing particulate activated carbon, an electrical conductive material and an adhesive agent and then forming by a green compact method, a calendaring method, a coating method, or a doctor blade method may be used. As the electrolyte, for example, an organic electrolyte prepared by dissolving tetraethylammonium tetrafluoroborate in propylene carbonate, or an organic electrolyte prepared by dissolving tetraethylphosphonium tetrafluoroborate in propylene carbonate, or the like may be used.

[0040]

A process for manufacturing the electric double layer capacitor will be briefly explained. First, collecting electrodes, electrodes, and separators as mentioned above are prepared. Then, a collecting electrode, an electrode, a separator, an electrode, and a collecting electrode are accumulated in this order, and such an accumulation is repeated, and then the resulting accumulated laminate is wound to form an electrodes-group.

[0041]

Subsequently, the electrodes-group and the organic electrolyte as mentioned above are incorporated into a case. Then, the case is sealed to obtain the capacitor. When the resins forming the above separator have a melting point or a carbonizing temperature of 300°C or more, the formed electrodes-group can be dried at a temperature of 150°C or more together with the collecting electrodes, the

electrodes, and the separators, before insertion into the case. When the resins forming ultrafine fibers of the above separator have a melting point or a carbonizing temperature of less than 300°C, the components are dried respectively, and then the electrodes-group is formed.

[0042]

A cell of the electric double layer capacitor may be a laminate type, a coin type, a cylindrical type, a prismatic type, or the like.

[EXAMPLES]

[0043]

The present invention now will be further illustrated by, but is by no means limited to, the following Examples.

[0044]

(Example 1)

A fiberizable solution (solid content concentration: 10wt%, viscosity: 1200 mPa·s) was prepared by dissolving polyacrylonitrile resin (softening temperature: 190 to 240°C, pyrolysis temperature: 350°C) in N,N-dimethyl-formamide.

[0045]

A fiberizing apparatus was prepared by connecting a syringe to a polytetrafluoroethylene tube, and attaching a stainless steel nozzle having an inner diameter of 0.6 mm at a tip of the tube. Then, the nozzle was connected to a high-voltage electric source. Further, a drum (collector, grounded) having a thin stainless steel plate with an electrically conductive fluorinated surface was placed at a position opposite to and separated from the nozzle (10 cm).

[0046]

Thereafter, the fiberizable solution was introduced into the syringe, and discharged therefrom by a microfeeder in a direction perpendicular to the direction of gravitational force (discharging amount 1 cc/hour), while the drum was rotated at a constant rate (surface velocity: 3.6 m/min), a voltage of +15 kV was applied to the nozzle from the high-voltage electric source to apply an electrical field to the discharged fiberizable solution so that the fiberizable solution was fiberized. The ultrafine fibers were collected on the thin stainless steel plate of the drum to form a ultrafine fibrous aggregate.

[0047]

Then, after a heat treatment at 160°C for 5 minutes, a separator of the present invention (mass per unit area: 3 g/m², thickness: 13 μm) composed of the ultrafine fibrous aggregate was obtained. In the separator, the ultrafine fibers constituting the separator were continuous, no bundle-like portion was observed, and the ultrafine fibers were dispersed and not substantially entangled.

[0048]

(Comparative Example 1)

A polyimide porous membrane (Ube Industries) was used as a separator.

[0049]

(Comparative Example 2)

The procedures as described in Example 1 was repeated, except that an amount of ultrafine fibers to be collected was increased, to prepare an ultrafine fibrous aggregate (mass per unit area: 6 g/m², thickness: 24 μm) as a separator.

[0050]

(Comparative Example 3)

First polyester fibers [fineness: 0.11 dtex (fiber diameter: 3.2 μm), fiber length: 5 mm, melting point: 260°C, softening temperature: 253°C, cross sectional shape: circle] composed of polyethylene-terephthalate and second polyester fibers [fineness: 0.2 dtex (fiber diameter: 4.3 μm), fiber length: 3mm, melting point: 260°C, softening temperature: 247°C, cross sectional shape: circle] composed of polyethylene-terephthalate were prepared.

[0051]

Subsequently, an aqueous slurry was prepared by dispersing the first polyester fibers and the second polyester fibers at a mass ratio of 70:30. Then, the aqueous slurry was supplied to a paper-making machine equipped with a cylinder, an inclined short wire Fourdrinier, a cylinder and a Yankee drier, respectively, to obtain wet webs. The resulting wet webs were laminated to form a laminated wet web, which was then dried by a Yankee drier heated at a temperature of 120°C.

[0052]

Thereafter, the dried laminated web was pressed at a linear pressure of 500 N/cm by passing through a pair of

heat calendars heated at a temperature of 200°C to obtain a wet-laid nonwoven fabric having a mass per unit area of 6 g/m², a thickness of 13 μm, and an apparent density of 0.45 g/cm³, which was used as a separator.

[0053]

(Evaluation of property of holding electrolyte)

Each separator sample cut into a disk shape (diameter: 30 mm) was placed at a temperature of 20°C and relative humidity of 65% to moisture equilibrium, and then the mass (M₀) was measured. Then, each separator sample was dipped in propylene carbonate for ten minute so that air in each separator sample was substituted by propylene carbonate, and the propylene carbonate was held. Thereafter, each separator sample was sandwiched between upper three filter papers (diameter: 30 mm) and lower three filter papers (diameter: 30 mm), and after the whole was pressed by a booster pump at a pressure of 1.6 MPa for 30 seconds, a mass (M₁) of each separator sample was measured.

[0054]

Then, a liquid-holding rate under pressure was calculated from the following equation. The measurement was conducted four times for each separator sample, and an arithmetic average thereof was a liquid-holding rate under pressure. The results are shown in Table 1.

Liquid-holding rate under pressure (%) = {(M₁-M₀)/M₀}×100

[0055]

As apparent from Table 1, the separator of the present invention has a very excellent holding electrolyte property. It was able to expect that, even if the expansions and shrinkages of capacitor electrodes are repeated with each charge and discharge cycle, the electrolyte in the separator is very little squeezed, and thus a life time of the capacitor can be prolonged.

[0056]

(Measurement of internal resistance)

As an electrode, a product prepared by kneading particulate activated carbon, carbon black, and polytetrafluoroethylene was prepared. Further, an aluminum foil as a collecting electrode, separators prepared in Example 1 and Comparative Examples 1 to 3 as separators, and a solution of tetraethylammonium tetrafluoroborate dissolved in propylene carbonate as an electrolyte were prepared.

Then, 10 capacitors of a coin cell shape were manufactured from the above materials, for each separator sample, respectively.

[0057]

Thereafter, an internal resistance of each capacitor was obtained from a charge and discharge curve measured by a charge and discharge tester. More particularly, it was obtained from the charge and discharge curve, which was obtained from an operation composed of a charging at a constant current of 1A for 2 minutes to 2.5 V and a discharging for 2 minutes. The results are shown in Table 1.

[0058]

As apparent from Table 1, the separators of the present invention had an internal resistance of 1.9 Ω , that is, an excellent ionic permeability.

[0059]

(Evaluation of property of preventing short circuit)

Ten coin cell capacitors used in the above item "Measurement of internal resistance" were manufactured for each sample. A percentage (fractional defective) of defective capacitors, which means a capacitor generating a short circuit after 100 charge and discharge cycles, was calculated. The results are shown in Table 1. The separators of the present invention exhibited an excellent property of preventing a short circuit, because they did not permeate electrode materials (carbon black or particulate activated carbon) which were dropped off due to the repeated expansions and shrinkages during the charging and discharging of the capacitor electrodes, and thus defective capacitors were not produced.

[0060]

[Table 1]

	Average fiber diameter	Ratio (Dd/Da)	Mass per unit area	Thickness	Apparent density	Tensile strength	Mean flow pore size	Maximum pore size	Liquid-holding rate under pressure	Internal resistance	Fractional defective	Comprehensive evaluation
Unit	μm		g/m^2	μm	g/cm^3	N/5mm	μm	μm	%	Ω	%	#
Example 1	0.2	0.2	3	13	0.23	0.53	0.55	1	250	1.9	0	◎
Comparative Example 1	—	—	11	18	0.61	9.1	0.2	10	15	3	0	△1
Comparative Example 2	0.2	0.2	6	24	0.21	0.6	0.45	1	250	2.5	0	△2
Comparative Example 3	3.4	0.1	6	13	0.45	3	21	65	10	2	50	x

: Comprehensive evaluation

◎ : Each of the property of holding an electrolyte, the property of preventing a short circuit, and the ionic permeability was more than excellent.

△1 : The ionic permeability was poor, and therefore application is limited.

△2 : The ionic permeability were bad, and designs such as an increased capacity are limited.

x : The property of holding an electrolyte was bad and the fractional defective was high, and therefore, it was impossible to use.

[DOCUMENT NAME] Abstract

[ABSTRACT]

[OBJECT] A separator for the electric double layer capacitor, having an excellent holding electrolyte property, and capable of satisfying both a property of preventing a short circuit and an ionic permeability, and an electric double layer capacitor containing the same, are provided.

[MEANS FOR SOLUTION] The separator for an electric double layer capacitor according to the present invention is characterized in that the separator is composed of an ultrafine fibrous aggregate prepared by an electrostatic spinning process, an average fiber diameter of ultrafine fibers constituting the ultrafine fibrous aggregate is 1 μm or less, and a thickness of the ultrafine fibrous aggregate is 20 μm or less. The electric double layer capacitor according to the present invention contains the separator.

[SELECTED DRAWINGS] None